

On the law of increase of entropy for nonequilibrium systems

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Abstract

Under the assumption of a smooth full phase-space distribution function we prove that the nonequilibrium entropy S which is considered as a functional of the distribution vector for an N -body system possesses a lower bound and therefore can not decrease. We also compute the rate of change of S , $\partial S/\partial t$, showing that this is non-negative and having a global minimum at equilibrium. As an application we obtain a generalization of the (Bhatnager-Gross-Krook) BGK relaxation model.

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I. INTRODUCTION

As it is known, the second law of Thermodynamics has been based on Kelvin's and Clausius's principles which establish that work can not be produced without spending energy. These principles are based on experiments but to my knowledge no theoretical derivation based on first principles has been given[1]. For an adiabatically isolated system the second law establishes that the entropy can not decrease and is maximum at equilibrium[2].

To provide a theoretical proof of the second law or the law of increase of entropy for an isolated system first it is necessary to properly define the nonequilibrium entropy which would coincide with the thermodynamic entropy at equilibrium.

The equilibrium entropy is a well established concept. According to Boltzmann the entropy of a microstate X of a macroscopic system is a number, $S_B(X) = k_B \log |\Gamma_{M(X)}|$, with $|\Gamma_M|$ being the volume of the region of the phase space Γ_M corresponding to the macrostate $M = M(X)$ and k_B is the Boltzmann constant. The macrostate M is all of a group of states Y such that $M(Y) = M(X) = M$. For Boltzmann, every adiabatically isolated system in its natural evolution moves towards an state of maximum disorder -the state of equilibrium, which corresponds with the greatest possible volume in phase space. Gibbs, on the other hand, defines entropy as a functional of the distribution function F in phase space, $S_G = -k_B \int F \ln F dX$, and both entropies coincide at equilibrium. Out of equilibrium the situation is more ambiguous, due to the fact that the Gibbs entropy is a constant of motion under the microscopic dynamic given through the Liouville equation, it has been thought that macroscopic processes require coarse-graining. This point was worked out first by Gibbs and P. Ehrenfest & T. Ehrenfest. On the other hand, some authors argue that the relevant entropy for understanding thermodynamic irreversibility is the Boltzmann entropy and not the Gibbs entropy [3]-[5].

In this scenario, unlike treatments based on the definition of coarse-grained entropies[6], here we propose a generalization of the fine-grained Gibbs entropy postulate in terms of the set of reduced distribution functions of the system, the distribution vector, as the nonequilibrium entropy of an N-body isolated system[7], [8]. Under the assumption of smooth phase-space densities we prove that this nonequilibrium entropy can not decrease and is not a constant of motion under the dynamic given through the BBGKY (Bogolyubov-Born-Green-Kirkwood-Yvon) hierarchy of equations[9]. Here, we assume smoothness to exclude

multifractal phase-space distributions which some simulations have shown[7].

It is a fact that the Liouville equation describes an incompressible flow of representative points in phase space, however this is not the case with respect to the BBGKY hierarchy. Additionally, unlike an incompressible flow a compressible flow produces entropy, thus in this fact resides the reason of the behavior of the entropy we propose . Moreover, this entropy coincides with the Thermodynamic entropy at equilibrium. Hence, we are able to compute the entropy production for an isolated system, which is non-negative (zero at equilibrium), therefore conferring the character of the nonequilibrium potential of the system to this entropy production. Is this a theoretical proof of the second law of Thermodynamics? it depends to the credit one gives to the nonequilibrium entropy we propose, nonetheless this is the closest definition to the microscopic dynamics of the isolated system we know.

We have structured the paper as follows. In section 2, we introduce the Hamiltonian dynamics of the N-body system obtaining the generalized Liouville equation. In section 3, we analyze the properties of the nonequilibrium entropy, compute the entropy production and obtain the kinetic equation for the one-particle reduced distribution function. Finally in section 4, we emphasize our main conclusions.

II. HAMILTONIAN DYNAMICS

We will consider a N-body system whose Hamiltonian results from the addition of a kinetic energy term and a term coming from the interaction between the particles

$$H = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + \frac{1}{2} \sum_{j \neq k=1}^N \phi(|\mathbf{q}_j - \mathbf{q}_k|) \quad , \quad (1)$$

with m being the mass of a particle, and $\phi(|\mathbf{q}_j - \mathbf{q}_k|) \equiv \phi_{jk}$ the interaction potential. Moreover, the equations of motion are

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i} \quad , \quad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i} \quad . \quad (2)$$

The statistical description of the system can be performed in terms of the full phase-space distribution function $F(x^N, t)$, where $x^N = \{x_1, \dots, x_N\}$ and $x_j = (\mathbf{q}_j, \mathbf{p}_j)$ or alternatively in terms of the distribution vector \mathbf{f} [9], both completely equivalent but the last more appropriated for nonequilibrium systems in order to show irreversibility. Here,

$$\mathbf{f} \equiv \{f_o, f_1(x_1, t), f_2(x^2, t), \dots, f_N(x^N, t)\} \quad (3)$$

is the set of all the s-particle reduced distribution functions, $s = 0, \dots, N$, where the s-particle reduced distribution functions

$$f_s = \frac{N!}{(N-s)!} \int F(x^N, t) dx_{s+1} \dots dx_N, \quad (4)$$

are obtained by integrating over $N - s$ particles with $f_o = 1$. The dynamics of the reduced distribution functions can be obtained from the Liouville equation

$$\frac{\partial}{\partial t} F = [H, F]_p, \quad (5)$$

where $[.,.]_p$ is the Poisson bracket, by using Eq. (4). One obtains the generalized Liouville equation[7]-[9]

$$\frac{\partial}{\partial t} \mathbf{f}(t) = \mathcal{L} \mathbf{f}(t), \quad (6)$$

which is a compact way of writing the BBGKY hierarchy of equations. In this equation, \mathcal{L} is the generalized Liouvillian whose diagonal part $\mathcal{P}\mathcal{L}$ is defined through[8]

$$\langle s | \mathcal{P}\mathcal{L} | s' \rangle = \delta_{s,s'} \left\{ \sum_{j=1}^s L_j^o + \sum_{j < n=1}^s L'_{j,n} \right\}, \quad (7)$$

where $|s\rangle$ represent the s-particle state defined through $\langle s | \mathbf{f} | x^s \rangle = f_s(x^s)$, with $x^s = \{x_1, \dots, x_s\}$, $s = 0, \dots, N$. The s-particle states have the property $\langle s | s' \rangle = \delta_{s,s'}$ such that $\sum_{s=0}^N |s\rangle \langle s| = 1$ constitutes the closure relation. Moreover, $L_j^o = [H_j^o, \dots]_P$, where $H_j^o = \mathbf{p}_j^2 / 2m$, and $L'_{j,n} = [H'_{j,n}, \dots]_P$, with $H'_{j,n} = \frac{1}{2} \phi_{j,n}$. In addition, the non-diagonal part $\mathcal{Q}\mathcal{L}$ is given by[8]

$$\langle s | \mathcal{Q}\mathcal{L} | s' \rangle = \delta_{s',s+1} \int \left\{ \sum_{j=1}^s L'_{j,s+1} \right\} dx_{s+1}. \quad (8)$$

Finally, in view of Eqs. (7) and (8) and using the properties of the s-particle states $|s\rangle$, by multiplying by $|x^s\rangle$ to the right and by $\langle s|$ to the left of (6) one obtains one of the components of the hierarchy

$$\frac{\partial}{\partial t} f_s - \sum_{j=1}^s L_j^o f_s - \sum_{j < n=1}^s L'_{j,n} f_s = \sum_{j=1}^s \int L'_{j,s+1} f_{s+1} dx_{s+1}, \quad (9)$$

where the right hand side is the collision term coupling f_s with f_{s+1} . In the case of $s = 1$ Eq. (9) reduces to

$$\frac{\partial}{\partial t} f_1 + \mathbf{p}_1 \frac{\partial}{\partial \mathbf{q}_1} f_1 = - \int \mathbf{F}_{1,2} \frac{\partial}{\partial \mathbf{p}_1} f_2 dx_2, \quad (10)$$

where $\mathbf{F}_{1,2} = -\nabla_1 \phi_{1,2}$ [10].

III. ENTROPY PRODUCTION AND IRREVERSIBILITY

Our statistical theory is based on the definition of the nonequilibrium entropy proposed in [7], [8]

$$\begin{aligned} S &= -k_B \text{tr} \{ \mathbf{f} \ln (\mathbf{f}_{eq}^{-1} \mathbf{f}) \} + S_{eq} \\ &= -k_B \sum_{s=1}^N \frac{1}{s!} \int f_s \ln \frac{f_s}{f_{eq,s}} dx_1 \dots dx_s + S_{eq} \end{aligned} \quad (11)$$

which generalizes the Gibbs entropy postulate, where S_{eq} is the equilibrium entropy coinciding with the thermodynamic entropy and \mathbf{f}_{eq} is the equilibrium distribution vector satisfying $\mathcal{L}\mathbf{f}_{eq} = 0$. The nonequilibrium entropy (11) reaches its maximum value $S = S_{eq}$ at the equilibrium state, when $\mathbf{f} = \mathbf{f}_{eq}$.

At this point, it should be clarified that a description of the system in terms of the full phase-space N-particle distribution function is justified for equilibrium systems for which the representative ensemble is distributed uniformly through the phase space. Nonetheless, the nonuniformity of nonequilibrium systems leads to a random clusterization caused by the interaction between different s-particle clusters, and the same global quantity may be obtained for an infinite number of realizations. This fact is taken into account in the BBGKY hierarchy[11] which explicitly incorporates the interaction between different s-particle clusters through the nondiagonal part $\mathcal{Q}\mathcal{L}$ of the generalized Liouvillian \mathcal{L} . The nonequilibrium system behaves as a random mixture of s-particle systems and, therefore the total entropy should be the sum of all the s-particle entropies. The randomness creates entropy as we will see later on.

More interestingly here is to establish the direction of change of this entropy in a natural process. To discern this we first note that since $f_s \ln f_s/f_{eq,s}$ is a convex function[12]

$$f_s \ln \frac{f_s}{f_{eq,s}} \geq f_s - f_{eq,s} \quad (\text{for } f_s \geq 0 \text{ and } f_{eq,s} > 0) \quad (12)$$

and due to the fact that f_s and $f_{eq,s}$ both are smooth phase-space densities in the s-particle phase space

$$\int f_s \ln \frac{f_s}{f_{eq,s}} dx_1 \dots dx_s \geq 0 . \quad (13)$$

Thus, given that f_s is bounded and since $f_{eq,s} > 0$ there must exist a constant C such that

$$\int f_s \ln \frac{f_s}{f_{eq,s}} dx_1 \dots dx_s \leq C , \quad (14)$$

for $s = 1, \dots, N$. Hence, a lower bound for the nonequilibrium entropy exists

$$0 > S - S_{eq} \geq -k_B \sum_{s=1}^N \frac{1}{s!} C, \quad (15)$$

which means that the nonequilibrium entropy (11) can not decrease. Consequently, the law of increase of entropy (*i.e.* the second law of thermodynamics) follows, constituting this result one of the goals of the present contribution.

The rate of change of the nonequilibrium entropy (11) or entropy production can be computed using Eqs. (6), giving

$$\begin{aligned} \frac{\partial S}{\partial t} = & -k_B \text{tr} \left\{ \frac{\partial \mathbf{f}}{\partial t} \ln (\mathbf{f}_{eq}^{-1} \mathbf{f}) \right\} = \\ & -k_B \text{tr} \{ \mathcal{L} \mathbf{f} \ln (\mathbf{f}_{eq}^{-1} \mathbf{f}) \} \quad , \end{aligned} \quad (16)$$

which according to Eq. (15) should be non-negative. In a more explicit way, after using Eq. (9), Eq. (16) can be written as

$$\frac{\partial S}{\partial t} = -\frac{1}{T} \sum_{s=1}^N \frac{1}{s!} \sum_{j=1}^s \int f_s \mathbf{p}_j \left(-k_B T \frac{\partial}{\partial \mathbf{q}_j} \ln f_{eq,s} + \sum_{j \neq i=1}^s \mathbf{F}_{j,i} + \mathcal{F}_j \right) dx_1 \dots dx_s \quad (17)$$

where $\mathcal{F}_j(x^s)$ is defined through $f_s(x^s) \mathcal{F}_j(x^s) = \int \mathbf{F}_{j,s+1} f_{s+1} dx_{s+1}$, T is the equilibrium kinetic temperature taking into account that the dependence of $f_{eq,s}$ in the velocities is given through a local Maxwellian and $\mathbf{F}_{j,i} = -\nabla_j \phi_{j,i}$.

The entropy production given through Eq. (17) vanishes at equilibrium when f_s coincides with $f_{eq,s}$. Moreover, because \mathbf{p}_j is arbitrary

$$\sum_{j \neq i=1}^s \mathbf{F}_{j,i} + \mathcal{F}_j^{eq} = k_B T \frac{\partial}{\partial \mathbf{q}_j} \ln f_{eq,s} \quad (18)$$

is sufficient to satisfy the extremum condition $\delta \dot{S} / \delta f_s |_{eq} = 0$, with $\dot{S} \equiv \partial S / \partial t$. Here, the right hand side of Eq. (18) is the mean force [13] and the left hand side is the sum of two parts, the first is the force due to the van der Waals interactions with the $s-1$ fixed particles different from the j -th particle in the s -th cluster (responsible for the compressions and dilatations of the s -th cluster), while the second is the average force on particle j -th by the remaining $N-s$ particles of the system. It is known that Eq. (18) gives rise to a hierarchy of equations the Yvon-Born-Green (YBG) hierarchy[9]. Now, by making use of

the extremum condition Eq.(18), we can rewrite the entropy production Eq. (17) as

$$\begin{aligned} \frac{\partial S}{\partial t} = & -\frac{1}{T} \frac{1}{s!} \sum_{j=1}^N \int f_s \mathbf{p}_j (\mathcal{F}_j - \mathcal{F}_j^{eq}) dx_1 \dots dx_s = \\ & -\frac{1}{T} \sum_{s=1}^N \frac{1}{s!} \sum_{j=1}^s \int (\Delta f_s + f_{eq,s}) \mathbf{p}_j (\mathcal{F}_j - \mathcal{F}_j^{eq}) dx_1 \dots dx_s , \end{aligned} \quad (19)$$

where $\Delta f_s = f_s - f_{eq,s}$. The right hand side of the last equal sign in Eq. (19) has two parts, the second of which involving $f_{eq,n}$, provided \mathcal{F}_j has even parity under time reversal, vanishes. It must be pointed out that \mathcal{F}_j has even parity if $f_{s+1}(x^{s+1}) = f_1(x_{s+1})f_s(x^s)$ which is a reasonable assumption in large enough time scales. Henceforth, after defining the nonequilibrium current $\mathbf{J}_j \equiv \Delta f_s \mathbf{p}_j$ which vanishes at equilibrium, Eq. (19) can be rewritten

$$\frac{\partial S}{\partial t} = -\frac{1}{T} \sum_{s=1}^N \frac{1}{s!} \sum_{j=1}^s \int \mathbf{J}_j (\mathcal{F}_j - \mathcal{F}_j^{eq}) dx_1 \dots dx_s . \quad (20)$$

In the previous equation (20) the term under the integral possesses the form of the product of a thermodynamic current \mathbf{J}_j times the corresponding conjugated thermodynamic force $(\mathcal{F}_j - \mathcal{F}_j^{eq})$, which constitutes the typical expression of the entropy production in Nonequilibrium Thermodynamics. At this point, following the standards of Nonequilibrium Thermodynamics[14], from Eq. (20) provided the existence of an equilibrium state is assumed, it follows

$$\mathbf{J}_i = - \sum_{j=1}^s \frac{\mathbf{L}_{ij}}{T} (\mathcal{F}_j - \mathcal{F}_j^{eq}) , \quad (21)$$

where \mathbf{L}_{ij} is a phenomenological coefficient which should be non-negative and having even parity or in terms of the related mobility $\mathbf{M}_{ij} = \mathbf{L}_{ij}/T f_s$

$$\mathbf{J}_i = - \sum_{j=1}^s f_s \mathbf{M}_{ij} (\mathcal{F}_j - \mathcal{F}_j^{eq}) . \quad (22)$$

The phenomenological relations (21) or (22) manifest the fact that a restoring current arises when the system deviates from equilibrium by the action of a thermodynamic force, this constituting a generalization of the Onsager's regression hypotesis[16]. Additionally, \mathbf{M}_{ij} might be a function of f_s and $\{\mathcal{F}_j\}$, $\mathbf{M}_{ij}(f_s, \{\mathcal{F}_j\})$ in general. Therefore, after substituting Eq. (22) into Eq. (20)

$$\frac{\partial S}{\partial t} = \frac{1}{T} \sum_{s=1}^N \frac{1}{s!} \sum_{i,j=1}^s \int f_s \mathbf{M}_{ij} (\mathcal{F}_j - \mathcal{F}_j^{eq})^2 dx_1 \dots dx_s \geq 0 . \quad (23)$$

To test our previous analysis, near equilibrium we can define an effective mobility $\mathbf{M}_{ij}^{eq} = \int \mathbf{M}_{ij} f_{eq,s} dx_1 \dots dx_s$, thus

$$\mathbf{J}_i = - \sum_{j=1}^s f_s \mathbf{M}_{ij}^{eq} (\mathcal{F}_j - \mathcal{F}_j^{eq}) \quad (24)$$

which by introducing the inverse mobility matrix ζ_{ij}^{eq} ($\sum_{j=1}^s \zeta_{ij}^{eq} \mathbf{M}_{jl}^{eq} = \delta_{il}$), the friction matrix, can be rewritten as

$$\begin{aligned} f_s (\mathcal{F}_i - \mathcal{F}_i^{eq}) &= - \sum_{j=1}^s \zeta_{ij}^{eq} \mathbf{J}_j = \\ &= - \sum_{j=1}^s \zeta_{ij}^{eq} \mathbf{p}_j (f_s - f_{eq,s}) . \end{aligned} \quad (25)$$

For $s = 1$, the previous equation allows us to derive from Eq. (10) the following kinetic equation for $f_1 \equiv f$

$$\frac{\partial}{\partial t} f + \mathbf{p} \frac{\partial}{\partial \mathbf{q}} f + k_B T \left(\frac{\partial}{\partial \mathbf{q}} \ln f_{eq} \right) \frac{\partial}{\partial \mathbf{p}} f = \zeta^{eq} \frac{\partial}{\partial \mathbf{p}} \mathbf{p} (f - f_{eq}) \quad (26)$$

constituting a generalization of the BGK [15] relaxation model containing the mean force and an extra acceleration term involving $\partial/\partial \mathbf{p} (f - f_{eq})$ which distinguishes this equation with respect to the original BGK.

IV. CONCLUSIONS

In the framework of the BBGKY description we have found a way of generalizing the Gibbs fine-grained entropy for an isolated N-body system leading to irreversibility. We have proved that the nonequilibrium entropy of an isolated N-body system defined as a convex functional of the distribution vector can not decrease and that the rate of change of this entropy is a non-negative quantity having a global minimum at equilibrium. As an application of those results, after computing the entropy production, following the methods of Nonequilibrium Thermodynamics we introduce a positively defined mobility matrix which relates the nonequilibrium current with the corresponding thermodynamic force enabling us to write the entropy production as a positively defined quadratic form. As a consequence of introducing the phenomenological law, we have obtained a generalization of the BGK relaxation model which contains the mean force and an extra acceleration term involving

$\partial/\partial\mathbf{p}(f - f_{eq})$. At this point it should be mentioned that the nonequilibrium thermodynamics analysis may be generalized to the phase space as done in the Mesoscopic Nonequilibrium Thermodynamics (MNET) [17].

It should be stressed that as we have shown a proper description of the nonequilibrium system might be given in terms of the distribution vector which evolves according to the generalized Liouville equation. The compressibility inherent to the BBGKY hierarchy leads to the randomness, so that the system can be thought either as a random mixture of s-particle systems or an interacting mixture of compressible fluids. Hence, this description brings about the correct macroscopic dynamics.

Due to the generality of our theory of irreversibility even the Boltzmann irreversible equation and hence the Boltzmann H-theorem are embedded in here, as was shown in a previous paper[8]. Moreover, a quantum formulation is possible, which will be shown elsewhere.

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